

Degradation of the organic molecules in the shallow subsurface of Mars due to irradiation by cosmic rays

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[1] Detection of the organic matter on Mars is one of the main goals of the future Martian landing missions. Yet, the degradation of organic molecules by cosmic ray irradiation on Mars is often ignored. We calculate the radiation dose accumulation rates from solar and galactic cosmic rays at various depths in the shallow Martian subsurface. We demonstrate that a 1-billion-year outcrop on Mars accumulates the dosage of ~ 500 MGy in the top 0–2 cm and ~ 50 MGy at 5–10 cm depths. We show that the preservation of ancient complex organic molecules in the shallow (~ 10 cm depth) subsurface of rocks could be highly problematic if the exposure age of a geologic outcrop would exceed 300 Myr. We demonstrate that more simple organic molecules with masses ~ 100 amu should have a good chance to survive in the shallow subsurface of rocks. Implications to the sampling strategy for the oncoming Martian missions are discussed. **Citation:** Pavlov, A. A., G. Vasilyev, V. M. Ostryakov, A. K. Pavlov, and P. Mahaffy (2012), Degradation of the organic molecules in the shallow subsurface of Mars due to irradiation by cosmic rays, *Geophys. Res. Lett.*, 39, L13202, doi:10.1029/2012GL052166.

1. Introduction and Background

[2] In November 2011 NASA launched the most ambitious and expensive mission to Mars – Mars Science Laboratory (MSL). MSL, unlike previous landers, will have a unique capability to drill into the solid Martian rock down to 5 cm and detect complex organic molecules with masses up to 535 amu [Mahaffy, 2008]. If some kind of carbon-based biosphere were present on the early wet warm Mars [Carr and Head, 2010] then it is reasonable to expect that some complex organic molecules could have been preserved in the ancient Martian geologic outcrops. Various organic molecular biomarkers have been detected in the terrestrial 2.7-Gyr-year-old Archean rocks [Summons *et al.*, 1999]. Given slow erosion rates [Golombek *et al.*, 2006], slow hydrologic cycle and lack of any significant tectonic activity on Mars, it might seem logical to assume that the preservation of complex organics in the ancient rocks on Mars would be even better than in the terrestrial Archean rocks.

However, Mars does have several key environmental factors that were never present on Earth in its entire history. Specifically, Mars had a thin variable atmosphere and lacked a global magnetic field for at least the last 3.5 billion years. Therefore, the Martian surface has been bombarded continuously by the energetic particles of the galactic and solar cosmic rays (GCRs and SCRs). It is pivotal to understand whether organic molecules could have survived at shallow depths in the solid Martian rocks for billions of years.

[3] Ionizing radiation is usually ignored in the context of sterilization of the Martian surface probably because the total energy flux from the galactic cosmic rays is ~ 10000 times smaller than the energy of the solar X-ray and EUV flux ($\lambda < 120$ nm) at the Martian orbit. Such direct energy comparison is somewhat misleading for two reasons. First, absorption of a UV photon may or may not result in the breakup of organic molecules because the energy of UV photons can be comparable to the bond energy (~ 10 eV) of the target organic molecule. In contrast, collisions with either GCRs/SCRs protons (with energies > 10 MeV) or any secondary cascade particles would always result in the destruction of the original organic compounds. Second, all UV radiation should be effectively absorbed in the first mm of any exposed rock surface [Cockell and Raven, 2004]. Photochemically produced atmospheric oxidants (H_2O_2) can react with organic compounds, but their diffusion into the solid rocks would be limited by the rocks' porosity [Bullock *et al.*, 1994]. Furthermore, if the rock pores were filled with ice then the penetration of atmospheric oxidants would be further impeded. GCRs can penetrate down to 1–2 meter below the surface regardless of rocks' chemical composition, porosity or ice content. Therefore, MSL's rock samples drilled from 0–5 cm depths would be well shielded from UV radiation but would be affected by cosmic rays.

[4] Effects of ionizing radiation on the biological molecules in cells have been studied extensively for decades [Kudryashov, 2008]. There have been numerous studies on the radiolysis and repolymerization of various organic polymers important to industry – polyethylene, polypropylene, cellulose etc. [Ivanov, 1992]. However, there have been very few experimental studies on the survival of the organic compounds under ionizing radiation for Martian applications. Specifically, Kminek and Bada [2006] studied effects of gamma ray irradiation of amino acids and determined that the radiolysis constants for various aminoacids increase linearly with their molecular weight. Iglesias-Groth *et al.* [2011] reported consistent values for the radiolysis constants using an indirect calorimetric method. Kminek and Bada estimated that it would be necessary to drill 1.5–2 meters in order to have a chance to detect 3 billion-year-old aminoacids on Mars. Dartnell *et al.* [2007a, 2007b] used Monte-Carlo simulations to calculate proper radiation dosages from GCR irradiation in

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the Martian soils of various surface densities, solar minimum and maximum conditions, different elevations etc. However, *Dartnell et al.* [2007a, 2007b] stopped short of calculating the actual age of the organic degradation at various depths. Furthermore, both *Kminek and Bada* [2006] and *Dartnell et al.* [2007a, 2007b] did not consider irradiation by SCR.

[5] Here we estimated the destruction rate of organic molecules due to irradiation of both GCRs and SCR in the top layer of the Martian surface rocks as a function of the rock's composition, density and atmospheric mass. We first calculated the radiation dose accumulation rates using the new version of the standard GEANT4 code (<http://geant4.cern.ch>) - an approach similar to *Dartnell et al.* [2007a, 2007b] but at a higher vertical resolution. Then, we used the calculated dose rates profiles and the radiolysis constants for aminoacids from *Kminek and Bada* [2006] to determine the time of exposure necessary to degrade organic molecules of various masses at different depths on Mars.

2. Method

[6] Our model consists of the two domains - the atmospheric column at the top and the rock column at the bottom. We assumed the average atmospheric density/temperature profile from *Lodders and Fegley* [1998]. We found that as long as the chemical composition and total atmospheric mass column are kept the same, the exact atmospheric density/temperature profile has minimal effect on the calculations of the radiation dose accumulation rates in the rock. The atmospheric domain was divided in 100 layers (1 km each). The rock column was divided in 500 layers by mass (2 g/cm² each). We have performed calculations for three different types of solids in the soil/rock column - pure Fe₂O₃ rock; pure ice; "standard" Martian rock. The "standard" Martian surface rock elemental composition was taken from *Lodders and Fegley* [1998, pp. 195–197] - f(O) = 0.34 g/g; f(Fe) = 0.293 g/g; f(Si) = 0.17 g/g; f(Al) = 0.045 g/g; f(Ca) = 0.05 g/g; f(S) = 0.02 g/g; f(Mg) = 0.05 g/g; f(Na) = 0.02 g/g; f(Ti) = 0.005 g/g; f(Cl) = 0.005 g/g; f(H) = 0.002 g/g. The densities of the "standard" and Fe₂O₃ rocks were assumed at 2 g/cm³ while the density of ice was kept at 1 g/cm³. Rocks were considered uniform without any pores of air.

[7] The incident flux and energy distribution of the GCRs at the top of the Martian atmosphere were adopted from *Webber and Lezniak* [1974, Figure 1]. Note that *Webber and Lezniak's* [1974] GCR spectra for particles with energies >1 GeV is in the excellent agreement with the recent observational data from PAMELA (payload for antimatter matter exploration and light-nuclei astrophysics) [*Adriani et al.*, 2011]. Just as *Dartnell et al.* [2007a, 2007b], we conservatively assumed that the total GCR flux at the Mars orbit is the same as at Earth's. The actual GCR flux at the Mars orbit should be higher than at Earth's, since Mars is further away from the Sun and the modulation effect by the heliosphere is weaker.

[8] SCR flux is highly variable on the short time scales (11 year cycle). The average SCR flux at the Earth's orbit (SCR_{Earth}) is estimated from the irradiated lunar soils at ~75 protons/cm²/sec for particles with energies >10 MeV [*Reedy and Marti*, 1991]. Thus SCR flux at the Mars orbit was assumed to be SCR_{Earth}/(R_{Mars}/R_{Earth})² = 33 protons/cm²/sec. The average energy (*E*) spectra of the incident SCR was assumed to be $\sim E^{-2.1}$ - such dependence was

derived by averaging spectra of the 107 solar flares observed over 1974–2001 [*Mottl and Nymmik*, 2007].

[9] At the first simulation step, cosmic ray particles are injected at the top of the atmosphere. Particles would loose their initial energy by ionizing atmospheric/rock atoms and molecules or by producing secondary particles. GEANT4 code (version GEANT 4.9.3) keeps track of the ionization losses as well as all the secondary cascade particles while the initial particle propagates through the atmosphere-rock column [*Agostinelli et al.*, 2003]. GEANT4 is based on the Monte Carlo method.

[10] In our calculations we considered GCR particles in the 20 MeV – 10000 GeV energy range, while SCR particles were assumed to have energies in the range of 1 MeV – 1 GeV. SCR particles with energies below 1 MeV would be absorbed in the atmosphere and would not reach the Martian surface. GCR particles with energies below 20 MeV would be effectively modulated by the heliosphere and would not reach even the Martian orbit. There are very few GCR particles with energies above 10000 GeV or SCR particles with energies above 1 GeV. We have considered only protons and He ions as the primary GCR particles at the top of the Martian atmosphere and neglected effects of the primary heavy ions. Contribution of the heavy ions (C, N, O, Fe etc.) in the total GCR incident particle flux is ~0.1% and we expect their contribution at ~1% in the total radiation dose accumulation rates in the surface rocks.

[11] For convenience of calculations we separated GCR and SCR particles in the energy intervals spanning an order of magnitude energy each. Particles of GCRs were grouped in 7 energy intervals, while SCR were grouped in 4. In each energy interval, a particle was picked with a random energy and direction and launched at the top of the atmospheric column. To achieve good statistics we had to launch 10⁴–2 × 10⁶ particles per interval. Particles were considered lost if their energy approached the ionization threshold (~100 eV) or if the particle escaped from the top of the atmospheric layer. In our calculations, we found that the back-scattered secondary particles which escaped from the atmosphere contained ~1% of the primary incident energy. GEANT4 calculates the energy deposited in the atmosphere-rock column for each particle in each model layer. Then, we integrated energies deposited per particle and converted them into radiation dose per year as a function of depth.

[12] We estimated the radiolysis constants (*k*) for organic molecules in 100–500 amu range by using the linear dependence of the radiolysis constants vs. molecular mass from *Kminek and Bada* [2006] - organic particle with mass of 100 amu was assigned a radiolysis constant *k*₁₀₀ = 0.12 MGy⁻¹ while a heavy molecule with mass of 500 amu was assigned the radiolysis constant *k*₅₀₀ = 0.68 MGy⁻¹. Knowing the radiation dose rates and using the estimated radiolysis constants, we calculated the exposure time necessary to degrade detectable amounts of complex organic molecules in the shallow subsurface.

[13] The complex organic biomarkers in the Archean kerogens have been detected at ppb levels. If the ancient warm wet Mars had a biosphere then we can hypothesize similar levels of biomarkers in the ancient Martian outcrops. The lowest limit for organic detection by MSL has been reported at the ppb or hundreds of ppt levels [*Mahaffy*, 2008]. Therefore, we assumed that if the initial abundance of the organic molecules on Mars has been decreased by a

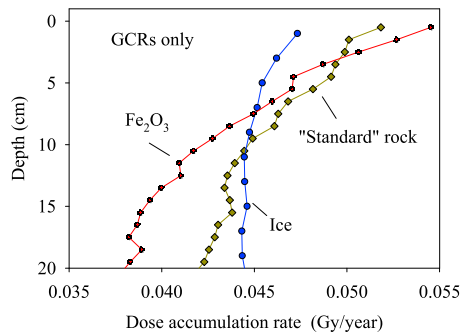


Figure 1. Radiation dose accumulation rates from GCRs vs. depth in various rocks and pure ice. GCRs flux during solar minimum was taken from *Webber and Lezniak*'s [1974]. The modern Martian atmosphere (7 mbar) was assumed above the surface. Top points are located in the middle of 0–1 cm rock layer. Lack of smoothness in the displayed curves is due to the nature of the Monte-Carlo numerical procedure. Smoother curves can be obtained by considering the larger number of incident GCR particles per each energy interval but that also increases the calculation time.

factor of 1000 due to ionizing radiation, then the organic compounds would be undetectable by MSL.

3. Results

[14] Figure 1 shows dose accumulation rate vs. depth for various rocks and ice if the top of the atmosphere has been bombarded by GCRs only. We found that the dose accumulation rate decrease with depth in all three materials (ice, Fe_2O_3 , “standard” rock). In contrast, *Dartnell et al.* [2007a, 2007b] reported a slight increase in the GCR's ionization rates with depth and the maximum of energy deposition from GCRs at depths of ~40–50 cm. They attributed such maximum in the energy deposition to the increasing flux of secondary cascade particles with increasing shielding depth in the soil until the depth of the Pfozter maximum. We found such maximum somewhat artificial for the Martian rocks because *Dartnell et al.* [2007a, 2007b] did not consider cosmic ray particles with energies below 100 MeV. In our calculations we included primary GCR particles with energies as low as 20 MeV. Low energy cosmic rays (20–100 MeV) cannot penetrate deep into the rock/ice and instead deposit their energy closer to the surface. Also, low energy cosmic rays do not produce a significant number of secondary particles. As a result the maximum radiation dose accumulation rate in our calculation almost always occurred at the surface (Figure 1). On Earth, low energy cosmic ray protons are effectively diverted by the Earth's magnetic field and the Pfozter maximum is indeed observed in the lower stratosphere.

[15] The absolute values of the dose accumulation rates in our calculations are about 30% less than *Dartnell*'s – see dose accumulation from GCR particles in pure ice Figure 1 (our study) vs. Figure 6 in *Dartnell et al.* [2007b]. There are several possible reasons for such a discrepancy. First, our spectra of GCR protons (adopted from *Webber and Lezniak* [1974]) at the Martian orbit are somewhat smaller than the spectra predicted by CREME96 model (used by *Dartnell*

et al. [2007a, 2007b]). Second, *Dartnell et al.* [2007a, 2007b] adopted a He/p ratio of ~14% for GCR particles of all energies. This assumption is valid only for the low-energy cosmic ray particles (<100 MeV/nuc). Instead, we used He/p ratios from *Webber and Lezniak* [1974]. *Webber and Lezniak*'s He/p ratio for GCR particles with energies of 1 GeV/nuc is ~10%, while for GCR particles with energies higher than 50 GeV/nuc, the He/p ratio is only ~3%. Therefore, in our calculations, there were smaller numbers of the GCR He ions. Third, *Dartnell et al.* [2007a, 2007b] took into account the contribution of heavy nuclei of the GCR particles by multiplying the proton dose accumulation rates by 1.37–1.42 factor. Such a factor is based on the assumption that the ionization produced by heavy nuclei ions can be calculated as the ionization produced by the independent nucleons. However, heavy particles have larger ionization cross-sections than independent nucleons and lose their energy more effectively. As a result, higher fraction of the heavier ions would be absorbed in the atmosphere. For example, in our simulations the He/p ratio decreases from the top of the Martian atmosphere to the Martian surface by 25%. Note that despite the discrepancy explained above, the magnitudes of the dose accumulation rates of GCRs in our study are in overall agreement with that of *Dartnell et al.* [2007a, 2007b].

[16] As shown on Figure 1, the chemical composition does not affect the dose accumulation rates significantly. “Standard” rock and Fe_2O_3 rock were assigned the same density (2 g/cm^3) and the difference in the dose accumulation rates did not exceed 7% down to 10 cm depths. The dose accumulation rate in ice is significantly higher than in rocks at lower depths due to the low density of ice, but at shallow depths (shallower than 20 cm) the differences in dose accumulation rates are small.

[17] Any previous studies of the dose accumulation rates on Mars neglected the contribution from SCRs. It was supposed that SCRs could not penetrate deep into the rock. and a significant fraction of SCRs would be absorbed in the atmosphere. We found that the contribution of SCRs to the total radiation dose accumulation rates is indeed minor comparing to the GCRs' under current Martian atmosphere (Figure 2). However, the total column mass of the Martian

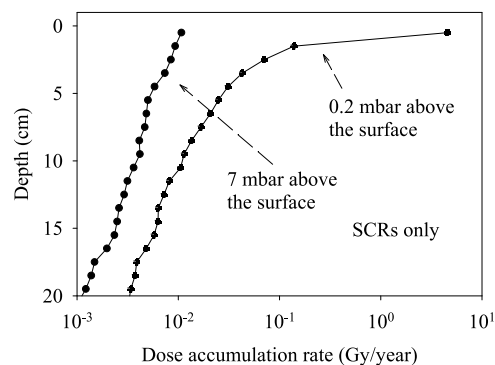


Figure 2. Radiation dose accumulation rates from SCRs vs. depth in the “standard” Martian surface rock (see Method section for the exact composition description). Calculations were conducted for the current (7 mbar) atmosphere and for the thin (0.2 mbar) atmosphere during low obliquity periods [*Armstrong et al.*, 2004].

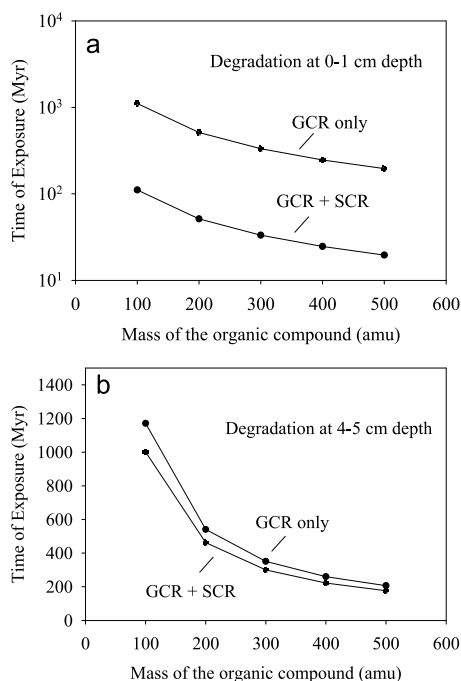


Figure 3. Exposure time (a) at 1 cm and (b) at 5 cm depths necessary for a 1000-fold decrease in the organic molecules abundance vs. molecular mass of the organic compounds. The “standard” Martian surface rock composition and 7 mbar atmosphere were assumed for calculations of GCRs contribution. Calculations of the organic degradation due to SCRs assume that the atmospheric pressure drops to 0.2 mb for 10% of Martian history in the last billion years [Armstrong *et al.*, 2004].

atmosphere could have been as low as 0.2 mbars during the periods of low obliquity [Armstrong *et al.*, 2004]. Our calculations showed that during periods of low atmospheric mass, SCRs radiation dose rates became by far the dominant source of ionization in the first 2 cm of the Martian surface rocks (Figure 2). To evaluate the average effect of SCRs, we assumed that 90% of its history the Martian atmosphere had been at 7 mbars or higher, while 10% of the time Mars had very little atmosphere (0.2–0.3 mbars). Therefore, the average radiation dose rate from SCRs was calculated by multiplying the dose rate for 0.2 mbar (Figure 2) by 0.1 and by adding dose rate for 7 mbar (Figure 2) multiplied by 0.9.

[18] Knowing the radiolysis constants (k) for specific molecules and dosage accumulation rates (I) at specific depths, we can calculate the exposure time for a 1000-fold-decrease in organic molecules abundance as: $T_{1000 \text{ decrease}} = (\ln(1000)/k)/I$. Figure 3a shows the time of exposure needed to produce a 1000-fold reduction in the concentration of organic molecules in the 0–1 cm rock layer below the surface. Our calculations suggest that it would take less than 50 million years to destroy organic molecules with masses larger than 200 amu in the top cm of the surface rocks. Whether it is a critical problem for MSL goals would depend on the surface erosion rates at the MSL’s landing site (Gale crater). The average erosion rate of the Gusev plains was reported at 0.03 nm/year [Golombek *et al.*, 2006]. At such slow rate, erosion would not be able to bring the “fresh” unexposed rock to the surface fast enough to avoid organic

degradation due to solar and galactic ionizing radiation. However, if the average erosion rate in the last 50 million years were closer to 1–10 nm/yr as suggested from Meridiani Planum data [Golombek *et al.*, 2006] then the top few centimeters of rock would not have enough exposure age to be affected by SCRs and GCRs.

[19] Figure 3b shows the time of exposure needed to decrease the abundance of organic molecules 1000-fold at 4–5 cm depths. SCRs produce noticeable but not the dominant contribution towards the degradation of organic molecules at 4–5 cm depths. We found that 100 amu organic molecules could be detectable at 4–5 cm depths even after 1 billion years of exposure to both SCRs and GCRs. Given that at least 3 cm of rock would be eroded in this period of time we conclude that 100 amu organic molecules have a decent chance of detection by MSL. In contrast, heavier organic molecules (300 amu and larger) decrease 1000-fold drop due to ionizing radiation in less than 300 Myr. Furthermore, the degradation rate due to GCRs at 20 cm depth decreases only by ~15% comparing to the degradation rate at 5 cm. Therefore, assuming even 1 nm/year average erosion rate, heavier organic molecules were likely to be degraded by ionizing radiation at the depths where the MSL is capable of drilling.

4. Discussion

[20] In our calculations we made a number of assumptions, which are listed in the auxiliary material.¹ Regardless of the premises, our estimates of the organic degradation on Mars should be viewed as conservative. The radiolysis constants from Kminek and Bada [2006] used in our calculations are most likely underestimated for Mars, because Kminek and Bada [2006] performed radiolysis experiments on the dry mixture of pure aminoacids in vacuum in closed glass vials. Therefore, it is inevitable that in the irradiated pure aminoacid mixture, there will be some repolymerization or crosslinking processes, which can reform originally destroyed aminoacids. In contrast, repolymerization and/or crosslinking of the organic molecules is a highly unlikely process on Mars, because organic matter is expected to be present in trace amounts in some mixture of silicates and iron oxides (see a special case of organic compounds in the organic-rich asteroids in auxiliary material).

[21] Furthermore, the experiments by Kminek and Bada [2006] could not include secondary oxidation processes of organic molecules from ionization of mineral matrix in the vicinity of organic matter. Regardless of the exact mineral composition of the Martian rock, collision of an energetic particle with SiO₂/iron oxide mineral matrix would produce O ions. Even if the original energetic particle had not broken organic molecules directly, O or OH radicals produced in the immediate vicinity of organic molecules are likely to break organic molecules (secondary oxidation). Bonner *et al.* [1985] found that the radiolysis constant for L-leucine mixed with dry amorphous silica (“syloid” in their study) is more than 100 times higher than the radiolysis constant of pure solid L-leucine. If the results of Bonner *et al.*’s study were to be confirmed for other organic molecules then, according to our calculations, it would take only millions of

¹Auxiliary materials are available in the HTML. doi:10.1029/2012GL052166.

years to degrade complex organic molecules in the shallow subsurface of Mars. That will pose a serious challenge for organic detection by MSL since its primary focus is to look for 3.5 billion-year-old organic biomarkers while only drilling 5 cm into the surface rock. Fortunately, there are several straightforward sampling strategies that would still allow the MSL to sample relatively “fresh” ancient rocks. One strategy would be to look for recent microcraters (1–10 m diameter) within the Gale crater. Fresh small craters have been detected at Martian mid-latitudes [Byrne *et al.*, 2009]. Another strategy would involve using the wheels of the MSL rover to dig into soft sedimentary rock prior to drilling. Given the size of the rover’s wheels such digging can provide samples from ~20 cm depths. Although a depth of 20 cm is not enough to avoid degradation by GCRs completely, it can slow down the rate of organic destruction by ~30% (see Figure 1) and will eliminate degradation associated with SCRs irradiation completely.

[22] Hypothetically, initial organic molecules could have been large (thousands of amu) and smaller organic molecules (100–500 amu) could have been derived by decomposition of larger ones later in Martian history. However, the radiolysis rate of the large molecules is much faster than the one for smaller ones [Kepner and Macey, 1968] and the survival of smaller organic compounds should not depend strongly on the mass of the initial large organic molecules.

5. Conclusions

[23] We find that the radiation dose accumulation rates from galactic cosmic ray particles are not very sensitive to the type of rock in the first 20 cm of the Martian regolith. We also find that the solar cosmic rays (SCRs) destroy organic compounds effectively in the first 2 cm of the Martian rock assuming that the atmospheric mass drops to 0.2 mbars for 10% of Martian history in the last billion years. Below 2 cm organic matter is destroyed primarily by the galactic cosmic rays (GCRs). We show that the preservation of the ancient complex organic molecules in the shallow (~10 cm depth) subsurface could be highly problematic if the exposure age of a geologic outcrop were to exceed 300 Myr. We demonstrate that more simple organic molecules with masses ~100 amu should survive in the shallow subsurface of Mars for ~1 billion years. Our calculations did not take into account secondary oxidation processes for organic molecules expected on Mars. Therefore, the realistic rates of the organic molecules destruction in the shallow subsurface of Mars could be even higher. Our calculations stress the importance of the “fresh” craters in the sampling strategy for the current MSL mission.

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